PATENT SPECIFICATION

NO DRAWINGS

Inventor: HUGH LEITHEAD ROBERTS

907,648

Date of filing Complete Specification Feb. 27, 1961.

Application Date March 17, 1960. *No. 9496/60.*

Complete Specification Published Oct. 10, 1962.

Index at acceptance: —Class 2(3), C1C(4:5:7B:8:11D).

International Classification: —C07c.

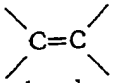
COMPLETE SPECIFICATION

Organic Sulphur Halogen Compounds

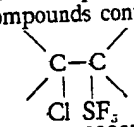
We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for making addition compounds of sulphur chloride pentafluoride and acetylenes.

In Specification No. 891,552 we have described reactions of sulphur chloride pentafluoride with olefines and other non-aromatic compounds containing the ethylenically unsaturated group.



in which addition takes place across the double bond to give compounds containing the group



In Application No. 39907/59 (Serial No. 905,066) we have described how by removing the elements of hydrogen chloride from addition products of sulphur chloride pentafluoride and olefines described in Specification No. 891,552 new compounds are obtained among which are some having the general formula $HC(SF_5):CClR$, in which R is hydrogen or an alkyl group.

We have now found that sulphur chloride pentafluoride will react with acetylene by adding across the treble bond to give unsaturated compounds having the general formula $HC(SF_5):CClR$.

According to our invention we provide a process for making compounds having the general formula $HC(SF_5):CClR$ where R may be hydrogen or an alkyl group, comprising subjecting a mixture of an acetylene and sulphur chloride pentafluoride to the action of heat or ultra-violet radiation, under an appropriate pressure which may be superatmospheric if desired.

One way of carrying out the reaction is to mix the acetylene and sulphur chloride pentafluoride in the gas phase at about 1 atmosphere pressure and to irradiate the mixture at room temperature with light from a mercury vapour lamp containing the 2537A line. Unreacted mixture may be recycled if required. This method is to be preferred when the acetylene is ordinary acetylene C_2H_2 in order to avoid the danger of explosion that accompanies compression of acetylene.

Where no explosion risk exists, as for example with propyne, an alternative way of carrying out the reaction is to introduce the mixture of the acetylene and sulphur chloride pentafluoride into a stainless steel pressure vessel, and to raise the temperature to 80° C. or higher, for example, up to 150° C., so that the reaction takes place under autogenous pressures of up to 50 atmospheres, for example, when using propyne, under autogenous pressures of 25 to 50 atmospheres. The reaction mixture may also, in similar cases where explosion risk is absent, be compressed before being introduced into the pressure vessel. Free-radical-producing catalysts, for example organic peroxides, may be added to the reaction mixture if desired.

The reaction products are washed with dilute aqueous alkaline solutions to remove acidic and other by-products, dried, for example over anhydrous magnesium sulphate, and purified by distillation.

EXAMPLE 1.

Propyne, $CH_3.C{\equiv}CH$, and sulphur chloride pentafluoride were mixed in equal volumes in the gaseous phase and the mixture introduced

into a reaction vessel irradiated with ultra-violet light from a mercury vapour lamp. A liquid product gradually collected in the vessel and after removal was washed with dilute caustic potash solution, then with water and saturated brine and finally dried over anhydrous magnesium sulphate. It nearly all distilled at 92° ± 1° and was shown by quantitative analysis to consist of the one to one adduct of propyne and sulphur chloride pentafluoride 2-chloropropenyl sulphur pentafluoride, $CH_3.CCl=CH.SF_5$.

Found	F 46.9; S 15.8;	Cl 17.5%
$C_3H_4SF_5Cl$ requires	F 44.4; S 16.4;	Cl 18.6%

The liquid showed infra-red absorption bands at wave numbers of 1660, 1100, 985, 895, and 871 cm^{-1}.

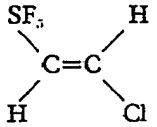
By treating the adduct $CH_3CCl=CH.SF_5$ with solid caustic potash or with caustic potash in petrol ether (100—120° C.) the elements of hydrochloric acid may be removed to give the pentafluorothio-substituted acetylene $CH_3C\equiv C.SF_5$.

EXAMPLE 2.

Propyne (20 g) and sulphur chloride pentafluoride (97 g.) were distilled into a stainless steel pressure vessel, heated to 90° C and maintained at this temperature for 4 hours. The maximum autogenous pressure developed was about 40 atmospheres, and this fell to about 25 atmospheres during the reaction. On cooling and releasing the pressure 47 g. of a pale yellow liquid was obtained, which after washing with dilute caustic potash and saturated brine and drying over anhydrous magnesium sulphate was distilled to give 25 g. of a colourless liquid identical with that obtained in the experiment of Example 1. About 8 g. of a higher boiling liquid remained behind.

EXAMPLE 3.

Acetylene (30 mls) purified from ketones and other impurities normally found in cylinder acetylene, and sulphur chloride pentafluoride (30 mls) were mixed in a reaction vessel irradiated with ultra-violet light as in Example 1. A colourless liquid gradually formed, which was shown by infra-red absorption analysis to be identical with the trans olefine



and to have principal bands at wave numbers of 1616, 918, 888, 874 and 852 cm^{-1}.

WHAT WE CLAIM IS:—

1. Process for making compounds having the general formula $HC(SF_5):CClR$, in which R may be hydrogen or an alkyl group comprising subjecting a mixture of an acetylene and sulphur chloride pentafluoride to the action of ultraviolet radiation, or to the action of heat in the presence if desired of a free-radical-producing catalyst, and if desired to the action of elevated pressure.

2. Process for making 2-chloro propenyl sulphur pentafluoride, $CH_3.CCl=CH.SF_5$, comprising subjecting a mixture of propyne and sulphur chloride pentafluoride to the action of ultra-violet radiation at room temperature, or heating it to temperatures in the range 80°—150° C. under autogenous pressures of 25 to 50 atmospheres.

ALFRED O. BALL,
Agent for the Applicants.

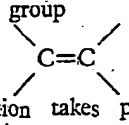
PROVISIONAL SPECIFICATION

Organic Sulphur Halogen Compounds

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to new compounds formed by addition of sulphur chloride pentafluoride to acetylenes.

In co-pending Application No. 31208/59 we have described reactions of sulphur chloride pentafluoride with olefines and other non-aromatic compounds containing the ethylenically unsaturated group



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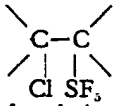
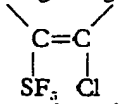


We have now found that sulphur chloride pentafluoride will react with acetylenes by adding across the treble bond to give unsaturated compounds containing the group



According to our invention we provide novel compounds of sulphur chloride pentafluoride with acetylenes, having the general formula $R^I.C(SF_5):CClR^{II}$ where R^I, R^{II} may be hydrogen or alkyl or aryl groups.

We also provide a process for making these novel compounds comprising subjecting a mix-

ture of an acetylene and sulphur chloride pentafluoride to heat or ultra-violet light, under an appropriate pressure which may be superatmospheric if desired.

One way of carrying out the reaction is to mix the acetylene and sulphur chloride pentafluoride in the gas phase at about 1 atmosphere pressure and to irradiate the mixture at room temperature with light from a mercury vapour lamp containing the 2537A line. Unreacted mixture may be recycled if required. This method is to be preferred when the acetylene is ordinary acetylene C_2H_2 in order to avoid the danger of explosion that accompanies compression of acetylene. Where no explosion risk exists an alternative way of carrying out the reaction is to introduce the mixture of acetylene and sulphur chloride pentafluoride into a stainless steel pressure vessel, and to raise the temperature to 100° C or higher so that the reaction takes place under autogenous pressure. The reaction mixture may also, in similar cases where explosion risk is absent, be compressed before being introduced into the pressure vessel.

The reaction products are washed with dilute aqueous alkaline solutions to remove acidic and other by-products, dried, for example over anhydrous magnesium sulphate, and purified by distillation.

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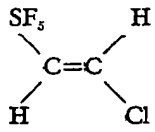

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Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1962.
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